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# Thermochemistry of phase transitions of aromatic amines: Estimation of the sublimation enthalpy at 298.15 K through the fusion enthalpy

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ABSTRACT

In the present work two methods of determination of sublimation enthalpies at 298.15 K based on solution enthalpies at 298.15 K and fusion enthalpies at the melting temperatures were applied for aromatic amines. The sublimation enthalpies of 17 substituted anilines and 1- and 2-naphthylamines at 298.15 K were calculated using their fusion enthalpies at the melting temperatures found in the literature, the solvation enthalpies in benzene and vaporization enthalpy of aniline. Additionally, the sublimation enthalpies of 9 substituted anilines and 1- and 2-naphthylamines were determined from their solution and solvation enthalpies. In this work we measured the solution enthalpies of aniline, its five derivatives and 2-naphthylamine in benzene while the solution enthalpies of other five aromatic amines were taken from the literature. The solvation enthalpies were calculated by means of the group-additivity scheme. The sublimation enthalpies values obtained as such were compared to the reference data. This method showed the good congruence with both direct experiment and solution calorimetry approach. In most cases the divergence does not exceed 2–3%. The consistency between independently determined sublimation enthalpies values validates the reliability of the relationship between the sublimation enthalpy at 298.15 K and fusion enthalpy at the melting temperature.



## 1. Introduction

Aromatic amines have been extensively used in the chemical industry for well over 150 years. They are applied for the production of polymers, azo dyes, rubber processing materials, herbicides, medicines, etc. The thermochemical data on the phase transitions of amines, in particular evaporation, solution and fusion enthalpies, are necessary for predict on of the solid-gas, solid-liquid and liquid-gas equilibria. The sublimation enthalpies of substituted anilines and naphthylamines were extensively studied in the works [1–27]. Various experimental techniques were employed in these studies, such as mass effusion Knudsen method [4,9–11,16–18,21], torsion-effusion technique [9,12,13,16,25], transpiration [1,3,14,24,27,28], thermogravimetric analysis [8], Calvet vacuum sublimation technique [5–7,10,19,20,22,23,26], static method [18], and gas chromatography [15].

A number of problems arise when the sublimation enthalpies are obtained with experimental measurements [29,30]. These problems include an inappropriate experimental setup, impurity of the samples, measurements of different polymorphic states. Thereby, indirect methods for determination of the sublimation enthalpy are useful for validation of experimental data.

Several empirical schemes have been recently applied for determination of the sublimation enthalpies of substituted anilines [30,31]. These schemes are based on a group-additivity of the sublimation enthalpy.

A solution calorimetry approach was also employed for determination of the sublimation enthalpies at 298.15 K of a number of aromatic amines [32] and showed good consistency with the conventional methods.

According to the solution calorimetry approach [32–35], the sublimation enthalpy at 298.15 K is determined as a difference between the solution enthalpy at 298.15 K measured experimentally and solvation enthalpy calculated from a group-additivity scheme [32]. The solution calorimetry approach has several advantages over the conventional methods, which can be crucial in the work with low volatile and unstable compounds. First, the experiment is carried out at the ambient temperature and does not lead to the thermal destruction of the compounds of interest. Note that it is also not necessary to adjust the results to 298.15 K. Second, the experiment has lower demand to the purity of the sample.

Recently we have developed a new approach which allows one to determine the sublimation enthalpy at 298.15 K by means of

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